

# PATENT SPECIFICATION

1.122.003



NO DRAWINGS

1.122.003

Date of Application and filing Complete Specification: 1 Oct., 1965.

No. 41819/65.

Application made in United States of America (No. 402,316) on 7 Oct., 1964.

Complete Specification Published: 31 July, 1968.

© Crown Copyright 1968

Index at acceptance:—C3 R(3D14A, 3D20, 3N1, 3N2, 3N7, 3P1)

Int. Cl.:—C 08 g 17/08

## COMPLETE SPECIFICATION

### Improvements in Aromatic Polycarbonates

We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, residing at 1 River Road, Schenectady 5, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new class of polymeric aromatic carbonate resins characterized by a high degree of hydrolytic stability and high heat distortion temperatures.

Because of their combination of good properties, aromatic carbonate polymers or resins derived from dihydric phenols such as 2,2 bis-(4-hydroxyphenyl)propane (bisphenol-A) have achieved wide commercial acceptance in the plastic industry. Generally speaking, such polycarbonates may be prepared by reacting the dihydric phenol with a carbonate precursor, such as phosgene, or diphenyl carbonate. The commercially available polycarbonate derived from bisphenol-A may be molded easily, possesses high impact and tensile strengths, and is characterized by a dimensional stability which surpasses that of any other commercially available thermoplastic material. However, in certain applications, the use of aromatic polycarbonates, such as bisphenol-A polycarbonate, has been limited due to the fact that they possess a poor hydrolytic stability. By "hydrolytic stability" is meant the ability of the polymer to withstand degradation or disintegration in aqueous environments as evidenced by weight loss.

In comparing the hydrolytic stabilities of carbonate polymers derived from different types of dihydric phenols, it has been recognized that the introduction of a methyl group ortho to the phenolic hydroxyl group (and, consequently, ortho to the carbonate group in the resulting polycarbonate) results in an improved hydrolytic stability. For example, a polycarbonate derived from 2,2 bis-(3-methyl-4-hydroxyphenyl)-propane (referred to as bisphenol-C) has a resistance to boiling in 10% aqueous sodium hydroxide solution which is about five times as good as the polycarbonate derived from bisphenol-A. Unfortunately, polycarbonates derived from bisphenol-C while being more hydrolytically stable, possess a considerably lower heat distortion temperature than bisphenol-A polycarbonates, and are therefore severely handicapped from a commercial standpoint.

It has not heretofore been possible to prepare commercially useful polycarbonates from tetra-alkyl alkylidene bisphenols, i.e., alkylidene bisphenols in which all four of the positions ortho relative to the two phenolic hydroxyl groups are substituted by alkyl groups. For example, the usual phosgenation method of polycarbonate preparation involving the passing of phosgene into a mixture of the tetra-alkyl alkylidene bisphenol, organic solvent, and acid acceptor consistently results in the production of a low molecular weight, (i.e., intrinsic viscosity less than 0.3), extremely brittle polycarbonate which is virtually useless as a thermoplastic molding compound. Introduction of other bisphenols, having a higher propensity to form high molecular weight polymers, into the reaction mixture containing the tetra-alkyl alkylidene bisphenols prior to phosgenation has also proved fruitless, since the resulting copoly-

[Price 4s. 6d.]

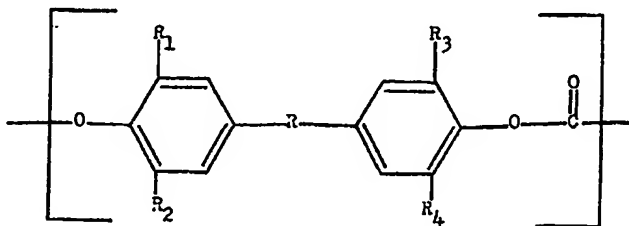
BEST AVAILABLE COPY

carbonate has a content of tetra-alkyl alkylidene bisphenol derived groups which is too low to affect the hydrolytic stability to any appreciable extent.

Accordingly high molecular weight, hydrolytically stable polymeric carbonates derived from tetra-alkyl alkylidene bisphenols which have heat distortion temperatures equal to those of bisphenol-A polycarbonate have heretofore been unavailable.

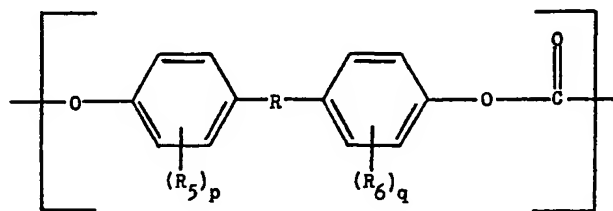
Unexpectedly, we have discovered a new class of high molecular weight, polymeric, aromatic carbonate compositions which are characterized not only by a superior hydrolytic stability but also by heat distortion temperatures which are at least equal to, and in most cases greater than those of bisphenol-A polycarbonates of equivalent molecular weight.

The present invention provides a high molecular weight, hydrolytically stable, polymeric aromatic carbonate having a heat distortion temperature of at least 150° C. and containing in its linear chain a major proportion of structural units of the formula

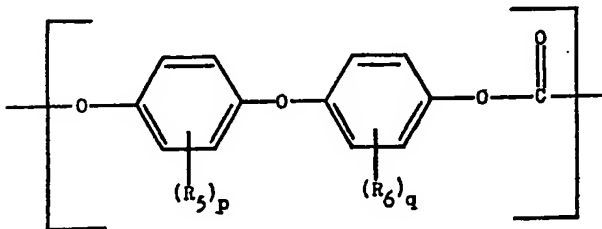


and a minor proportion of structural units of the formula

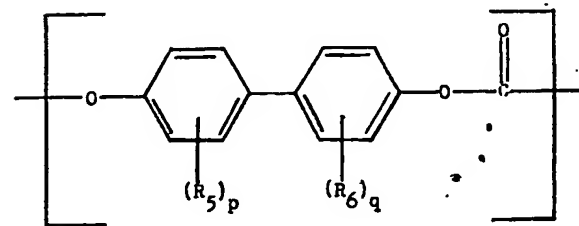
(a)



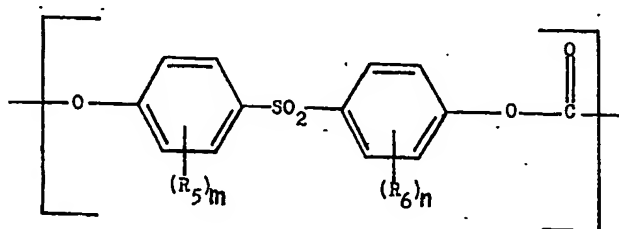
(b)



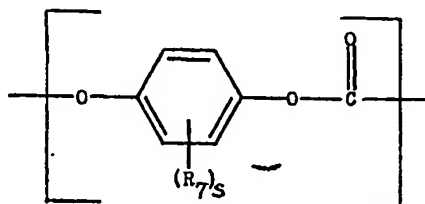
(c)



(d)



(e)



where

R is an alkylidene radical containing from 1 to 10 carbon atoms or a cycloalkylidene radical containing from 5 to 8 carbon atoms in the cyclic ring;

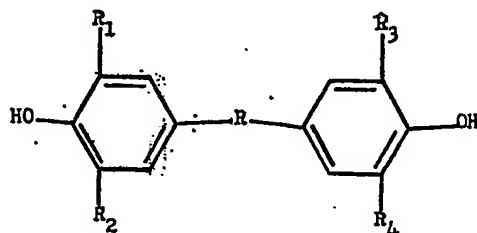
R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> may be the same or different and each is an alkyl radical containing from 1 to 3 carbon atoms;

R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> may be the same or different and each is halogen or an alkyl radical containing from 1 to 3 carbon atoms;

each of p and q is 0, 1 or 2 except that where R<sub>5</sub> and R<sub>6</sub> are both alkyl, each of p and q is 0 or 1;

and each of m, n and s is 0, 1 or 2.

The high molecular weight, high heat distortion temperature, hydrolytically stable, polymeric aromatic carbonates of the present invention may be produced by a process which comprises reacting, in an inert organic solvent containing an acid acceptor, a molar excess of a carbonyl halide with a tetra-alkyl alkylidene bisphenol of the formula



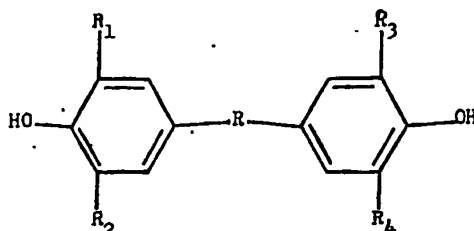
where

R is an alkylidene radical containing from 1 to 10 carbon atoms, or a cycloalkylidene radical containing from 5 to 8 carbon atoms in the cyclic ring, and

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are as defined above, to provide a low molecular weight carbonate polymer of said tetra-alkyl alkylidene bisphenol, and subsequently reacting said low molecular weight carbonate polymer with a dihydric phenol capable of reacting therewith described in detail hereinafter in the presence of sufficient carbonyl halide to complete the reaction to the desired extent. The presence of sufficient carbonyl halide for the last mentioned reaction step may be assured by adding further carbonyl halide (see, for example, Examples 3, 4 and 9 to 11 below) or by using up unreacted carbonyl halide remaining after the low molecular weight polymer has been formed in the first reaction step (see, for example, Examples 1, 2, 5 to 8 and 12 below).

By "tetra-alkyl alkylidene bisphenol" is meant bisphenols having the formula

(II)

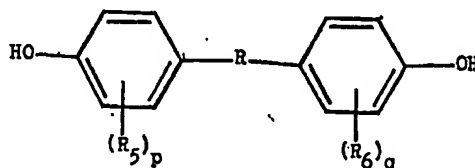


wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> all have the meanings given above. Examples of bisphenols falling within the above formula which may be employed to provide the polymeric carbonates of the present invention are:

- |    |   |    |
|----|---|----|
| 5  | 1,1-bis(3,5-dimethyl-4-hydroxyphenyl)-methane,<br>1,1-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-methane,<br>1,1-bis(3,5-diethyl-4-hydroxyphenyl)-methane,<br>1,1-bis(3,5-disopropyl-4-hydroxyphenyl)-methane,   | 5  |
| 10 | 1,1-bis(3,5-dimethyl-4-hydroxyphenyl)-ethane,<br>1,1-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-ethane,<br>1,1-bis(3,5-diethyl-4-hydroxyphenyl)-ethane,<br>1,1-bis(3,5-disopropyl-4-hydroxyphenyl)-ethane,   | 10 |
| 15 | 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-propane,<br>2,2-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-propane,<br>2,2-bis(3,5-diethyl-4-hydroxyphenyl)-propane,<br>2,2-bis(3,5-disopropyl-4-hydroxyphenyl)-propane,   | 15 |
| 20 | 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-butane,<br>2,2-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-butane,<br>2,2-bis(3,5-diethyl-4-hydroxyphenyl)-butane,<br>2,2-bis(3,5-diisopropyl-4-hydroxyphenyl)-butane,  | 20 |
| 25 | 3,3-bis(3,5-dimethyl-4-hydroxyphenyl)-pentane,<br>3,3-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-pentane,<br>3,3-bis(3,5-diethyl-4-hydroxyphenyl)-pentane,<br>3,3-bis(3,5-diisopropyl-4-hydroxyphenyl)-pentane,  | 25 |
| 30 | 3,3-bis(3,5-dimethyl-4-hydroxyphenyl)-hexane,<br>3,3-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-hexane,<br>3,3-bis(3,5-diethyl-4-hydroxyphenyl)-hexane,<br>3,3-bis(3,5-disopropyl-4-hydroxyphenyl)-hexane,   | 30 |
| 35 | 4,4-bis(3,5-dimethyl-4-hydroxyphenyl)-heptane,<br>4,4-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-heptane,<br>4,4-bis(3,5-diethyl-4-hydroxyphenyl)-heptane,<br>4,4-bis(3,5-diisopropyl-4-hydroxyphenyl)-heptane,  | 35 |
| 40 | 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-octane,<br>2,2-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-octane,<br>2,2-bis(3,5-diethyl-4-hydroxyphenyl)-octane,<br>2,2-bis(3,5-diisopropyl-4-hydroxyphenyl)-octane,<br><br>2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-nonane,<br>2,2-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-nonane,<br>2,2-bis(3,5-diethyl-4-hydroxyphenyl)-nonane,<br>2,2-bis(3,5-disopropyl-4-hydroxyphenyl)-nonane,<br><br>2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-decane,<br>2,2-bis(3-methyl-5-ethyl-4-hydroxyphenyl)-decane,<br>2,2-bis(3,5-diethyl-4-hydroxyphenyl)-decane,<br>2,2-bis(3,5-diisopropyl-4-hydroxyphenyl)-decane. | 40 |

As indicated above, any of the dihydric phenols described hereinafter which are capable of reacting with the reaction product of the tetra-alkyl alkylidene bisphenol and any further carbonyl halide necessary to complete the reaction, e.g. phosgene, to the extent necessary to provide a high molecular weight, high heat distortion temperature polymeric carbonate, may be employed in the practice of the invention. One class of suitable dihydric phenols is the alkylidene and cycloaliphatic bisphenols conforming to the formula

(III)



where R has the meaning given above; each of  $R_5$  and  $R_6$  is selected from halogen, such as fluorine, chlorine and bromine, and alkyl radicals containing up to three carbon atoms, i.e. methyl, ethyl, propyl, and isopropyl; each of p and q is 0, 1 or 2, except that when  $R_5$  and  $R_6$  are both alkyl, p and q are no greater than 1. Examples of bisphenols falling within the scope of the above formula III are:

1,1-bis(4-hydroxyphenyl)-methane,  
1,1-bis(3-methyl-4-hydroxyphenyl)-methane,  
1,1-bis(3,5-dichloro-4-hydroxyphenyl)-methane,  
1,1-bis(3,5-dibromo-4-hydroxyphenyl)-methane,

1,1-bis(4-hydroxyphenyl)-ethane,  
1,1-bis(3-methyl-4-hydroxyphenyl)-ethane,  
1,1-bis(3,5-dichloro-4-hydroxyphenyl)-ethane,  
1,1-bis(3,5-dibromo-4-hydroxyphenyl)-ethane,

2,2-bis(4-hydroxyphenyl)-propane,  
2,2-bis(3-methyl-4-hydroxyphenyl)-propane,  
2,2-bis(3,5-dichloro-4-hydroxyphenyl)-propane,  
2,2-bis(3,5-dibromo-4-hydroxyphenyl)-propane,

2,2-bis(4-hydroxyphenyl)-butane,  
2,2-bis(3-methyl-4-hydroxyphenyl)-butane,  
2,2-bis(3,5-dichloro-4-hydroxyphenyl)-butane,  
2,2-bis(3,5-dibromo-4-hydroxyphenyl)-butane,

3,3-bis(4-hydroxyphenyl)-pentane,  
3,3-bis(3-methyl-4-hydroxyphenyl)-pentane,  
3,3-bis(3,5-dichloro-4-hydroxyphenyl)-pentane,  
3,3-bis(3,5-dibromo-4-hydroxyphenyl)-pentane,

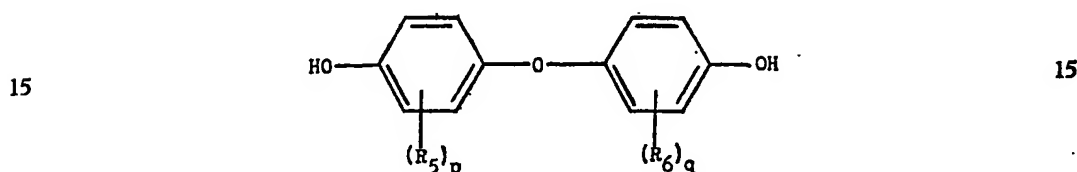
3,3-bis(4-hydroxyphenyl)-hexane,  
3,3-bis(3-methyl-4-hydroxyphenyl)-hexane,  
3,3-bis(3,5-dichloro-4-hydroxyphenyl)-hexane,  
3,3-bis(3,5-dibromo-4-hydroxyphenyl)-hexane,

4,4-bis(4-hydroxyphenyl)-heptane,  
4,4-bis(3-methyl-4-hydroxyphenyl)-heptane,  
4,4-bis(3,5-dichloro-4-hydroxyphenyl)-heptane,  
4,4-bis(3,5-dibromo-4-hydroxyphenyl)-heptane,

2,2-bis(4-hydroxyphenyl)-octane,  
2,2-bis(3-methyl-4-hydroxyphenyl)-octane,  
2,2-bis(3,5-dichloro-4-hydroxyphenyl)-octane,  
2,2-bis(3,5-dibromo-4-hydroxyphenyl)-octane,

- 2,2-bis(4-hydroxyphenyl)-nonane,  
 2,2-bis(3-methyl-4-hydroxyphenyl)-nonane,  
 2,2-bis(3,5-dichloro-4-hydroxyphenyl)-nonane,  
 2,2-bis(3,5-dibromo-4-hydroxyphenyl)-nonane,
- 5      2,2-bis(4-hydroxyphenyl)-decane,  
 2,2-bis(3-methyl-4-hydroxyphenyl)-decane,  
 2,2-bis(3,5-dichloro-4-hydroxyphenyl)-decane,  
 2,2-bis(3,5-dibromo-4-hydroxyphenyl)-decane,
- 10      1,1-bis(4-hydroxyphenyl)-cyclopentane,  
 1,1-bis(4-hydroxyphenyl)-cyclohexane,  
 1,1-bis(4-hydroxyphenyl)-cycloheptane,  
 1,1-bis(4-hydroxyphenyl)-cyclooctane.

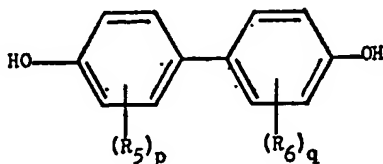
Another class of suitable dihydric phenols is the dihydric phenol ethers conforming to the formula  
 (IV)



where  $R_5$ ,  $R_6$ ,  $p$  and  $q$  all have the meanings given above. Examples of bisphenols falling within the scope of formula IV are:

- 20      bis-(4-hydroxyphenyl)-ether,  
 bis-(3-methyl-4-hydroxyphenyl)-ether,  
 bis-(3-ethyl-4-hydroxyphenyl)-ether,  
 bis-(3,5-dichloro-4-hydroxyphenyl)-ether,  
 bis-(3,5-dibromo-4-hydroxyphenyl)-ether,  
 bis-(3-chloro-5-methyl-4-hydroxyphenyl)-ether.

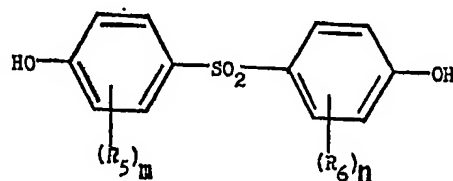
25      Still another class of dihydric phenols is the dihydroxydiphenyls conforming to the formula  
 (V)      25



where  $R_5$ ,  $R_6$ ,  $p$  and  $q$  all have the meanings given above. Examples of bisphenols falling within the scope of formula V are:

- 30      p,p'-dihydroxydiphenyl,  
 3,3'-dimethyl-4,4'-dihydroxydiphenyl,  
 3,3'-diethyl-4,4'-dihydroxydiphenyl,  
 3,3'-dichloro-4,4'-dihydroxydiphenyl,  
 3,3'-5,5'-tetrabromo-4,4'-dihydroxydiphenyl.
- 35      Yet, another class of dihydric phenols is the dihydroxyaryl sulfones conforming to the formula      35

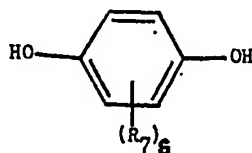
(VI)



where  $R_5$  and  $R_6$  have the meanings given above and each of  $m$  and  $n$  is 0, 1 or 2. Examples of bisphenols falling within the scope of formula VI are:

- |    |   |    |
|----|---|----|
| 5  | bis-(4-hydroxyphenyl)-sulfone,                  |    |
|    | bis-(3-methyl-4-hydroxyphenyl)-sulfone,         | 5  |
|    | bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfone,     |    |
|    | bis-(3,5-dibromo-4-hydroxyphenyl)-sulfone,      |    |
|    | bis-(3-chloro-4-hydroxyphenyl)-sulfone,         |    |
| 10 | bis-(3-methyl-5-ethyl-4-hydroxyphenyl)-sulfone, |    |
|    | bis-(3,5-diisopropyl-4-hydroxyphenyl)-sulfone.  | 10 |

A further class of dihydric phenols is the dihydroxy benzenes conforming to the formula (VII)



- |    |   |    |
|----|---|----|
| 15 | where   |    |
|    | $R_7$ is selected from halogen and alkyl radicals containing from 1 to 3 carbon | 15 |
|    | atoms, i.e. methyl, ethyl, propyl, and isopropyl; and                           |    |
|    | $s$ is 0, 1 or 2.   |    |
|    | Examples of such dihydroxy benzenes are:  |    |
| 20 | hydroquinone,   |    |
|    | 1,4-dihydroxy-2-chlorobenzene,  | 20 |
|    | 1,4-dihydroxy-2-bromobenzene,   |    |
|    | 1,4-dihydroxy-2,3-dichlorobenzene,  |    |
|    | 1,4-dihydroxy-2-methylbenzene,  |    |
| 25 | 1,4-dihydroxy-2,3-dimethylbenzene,  |    |
|    | 1,4-dihydroxy-2-bromo-3-propylbenzene.  | 25 |

The carbonyl halide used to prepare the polymeric carbonates of the invention may be carbonyl bromide, or carbonyl chloride. Carbonyl chloride (phosgene) is preferred due to its availability and low cost.

- |    |   |    |
|----|---|----|
| 30 | A molar excess of carbonyl halide, based upon the total moles of tetra-alkyl alkylidene bisphenol charged to the reaction mixture, should be used. In this connection we have found a 5 to 10% molar excess to be sufficient. | 30 |
|----|---|----|

- |    |  |    |
|----|--|----|
| 35 | The reaction between the carbonyl halide and the tetra-alkyl alkylidene bisphenol in accordance with the invention is preferably conducted in an organic solvent for the high molecular weight polymeric carbonate to be formed, which solvent is inert in the sense that it does not enter into the polymerization reaction and does not deleteriously affect the formed polymer. Examples of suitable inert organic solvents are methylene chloride, ethylene dichloride, dioxane, and chlorobenzene. The acid acceptor employed in the reaction between the carbonyl halide and the tetra-alkyl alkylidene bisphenol should, in general, be a tertiary amine, such as pyridine, for example, which is preferred due to its availability and relatively low cost. Examples of other tertiary amines suitable for use in this connection are triethylamine, N,N-dimethylaniline, N,N-diethylaniline and N-methylpiperidine. | 35 |
| 40 |  | 40 |

A preferred method for preparing the polymeric carbonates of the invention involves, first, slowly passing phosgene gas into a reaction mixture containing the tetra-alkyl alkylidene bisphenol, the inert organic solvent (such as methylene chloride), and pyridine. Phosgenation should be continued until about a 5—10% molar excess of phosgene (based upon the moles of bisphenol) has been added.

The temperature at which such phosgene reaction may proceed may vary from about 0° C. to about 100° C., although, generally speaking, the reaction proceeds satisfactorily at room temperature (25° C.) to 50° C. Since the reaction is exothermic, the rate of phosgene addition may be used to control the reaction temperature. The phosgene may first be dissolved in a quantity of inert organic solvent and the resulting phosgene solution added slowly, with stirring, to the reaction mixture containing the bisphenol and acid acceptor.

After the molar excess of phosgene has been added to the reaction mixture, the dihydric phenol may be introduced. This may be accomplished by forming a solution of the dihydric phenol in an inert-organic-solvent-pyridine mixture which may then slowly be added, with stirring, to the phosgenated reaction mixture. To ensure a complete reaction, and to provide the maximum yield of desired polymeric carbonate, the reaction mixture resulting after the addition of the dihydric phenol solution may be phosgenated until maximum solution viscosity is obtained.

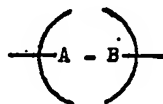
The amount of dihydric phenol added to the phosgenated reaction mixture may vary to a large extent. Less than one mole of dihydric phenol is added per mole of tetra-alkyl alkylidene bisphenol originally charged to the reaction mixture, so that the resulting high molecular weight, polymeric carbonate contains a major proportion of tetra-alkyl-alkylidene-derived carbonate units in its linear chain.

The resulting high molecular weight, polymeric carbonate may be separated easily from the final reaction mixture in a number of ways, as for example, by precipitation by the addition of an aliphatic hydrocarbon non-solvent, such as pentane, hexane, heptane and mixed petroleum spirits with boiling points sufficiently different from the polymer solvent used to enable easy separation by distillation. Alternatively, the polymer may be recovered by the addition, to the reaction mixture, of aliphatic alcohol non-solvents such as methanol, ethanol, isopropanol, or n-propanol, or simply by evaporating the polymer solution to dryness.

The total amount of inert organic solvent employed, i.e., the amount originally charged to the reaction mixture containing the tetra-alkyl alkylidene bisphenol, and the amount, if any, added with the introduction of the dihydric phenol, is not critical. It is only necessary that a sufficient amount of solvent be used to dissolve all of the high molecular weight, polymeric carbonate present at the conclusion of the reaction so as to permit an easy separation of the desired polymer from the final reaction mixture. Ordinarily, sufficient inert organic solvent is used to provide a 5—20% solution of the polymeric carbonate in the inert organic solvent, or for about 5 to about 20 times by weight as much inert organic solvent as tetra-alkyl alkylidene bisphenol originally charged to the reaction mixture. In the event the polymer solution obtained is too viscous to facilitate easy separation of the polymer, it is, of course, possible to add more organic liquid to the reaction mixture.

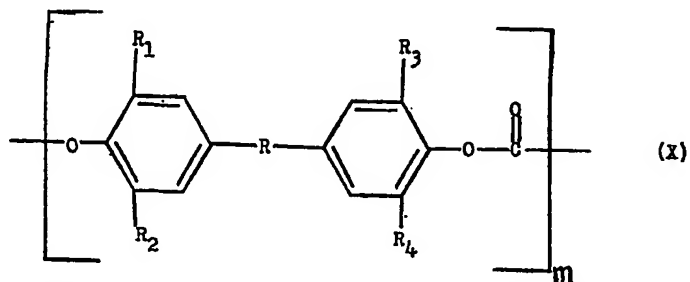
In the event a single tetra-alkyl alkylidene bisphenol is used in the original reaction mixture and a single dihydric phenol of the type described above is added subsequent to the phosgenation thereof, the resulting polymer will be a copolymeric polycarbonate possessing recurring blocks of the formula

(IX)



where A is a radical of the formula

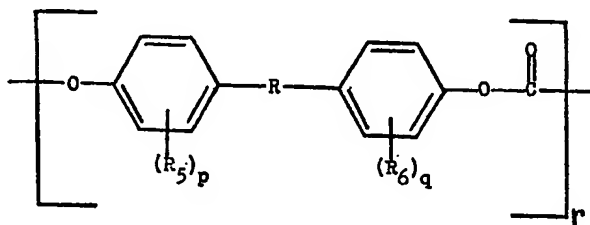




where R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> all have the meanings given above; m is a whole number from 15 to 25 (i.e., in the average block A the total number of structural tetra-alkyl alkylidene units will range from 15 to 25); and B is a coupling radical selected from

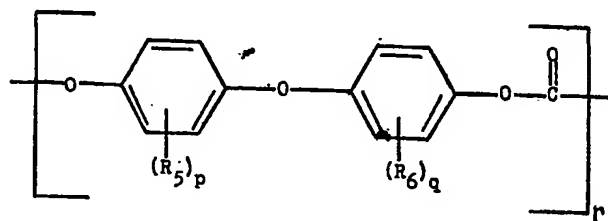
(a)

5

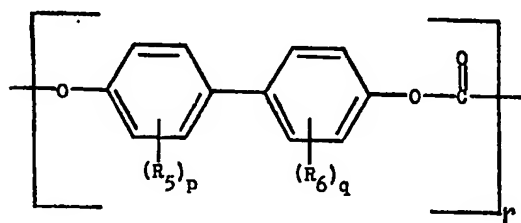


5

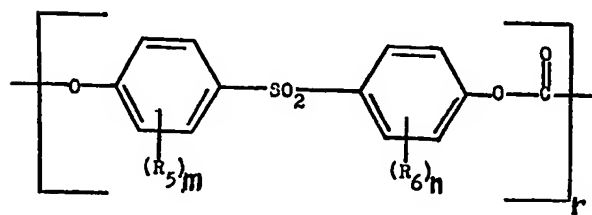
(b)



(c)

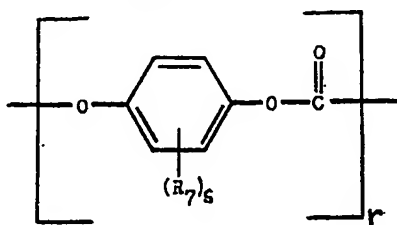


(d)



(e)

and



where  $R_1, R_2, R_3, R_4, R_5, R_6, R_7, m, n, p, q$  and  $s$  all have the meanings given above, and  $r$  is a whole number from 1 to 10.

Thus, if a single tetra-alkyl alkylidene bisphenol is originally employed, and a single dihydroxy compound is used, the final carbonate polymer will be a copolymeric polycarbonate consisting of homopolymeric blocks of formula (X) joined together by a coupling radical selected from the group (a), (b), (c), (d) and (e) set forth above.

Whether the coupling radical is monomeric (i.e.,  $r$  is equal to 1), or is polymeric (i.e.,  $r$  is greater than 1) will depend upon whether there was enough residual phosgene present in the phosgenated reaction mixture to which the dihydroxy compound was added to cause the dihydroxy compound to become polymerized by reacting with such phosgene before it was able to link two of the polymeric blocks of formula X to form the high molecular weight, polymeric carbonate of the invention. Also, a post phosgenation of the reaction mixture into which the dihydroxy compound has been added may result in some polymerization of that compound by reaction with phosgene before it was able to link two of the polymeric blocks of formula X. Whether the coupling radical in the final high molecular weight polymeric carbonate of the invention be monomeric or polymeric is unimportant excepting, of course, that the resulting high molecular weight polymeric carbonate have the requisite high heat distortion temperature and hydrolytic stability.

Should two or more different types of tetra-alkyl alkylidene bisphenols be charged to the original reaction mixture, the resulting polycarbonate will contain blocks —D— where D is a random copolymer composed of structural units derived from the two or more tetra-alkyl alkylidene bisphenols used, which structural units are joined together through carbonate linkages to form the block. In the average block, the total number of such structural tetra-alkyl alkylidene bisphenol derived units will range from 15 to 25. The blocks —D— will be joined together to form the high molecular weight polymers of the invention by a connecting radical —E— which will consist of one of the radicals (a), (b), (c), (d) or (e) set forth above, or a mixture of two or more of such radicals, depending upon whether more than one kind of dihydroxy compound is introduced into the phosgenated reaction mixture.

Thus, the use of the dihydroxy compound set forth above in the practice of the invention results in the production of copolymeric carbonates which may be described as comprising polymeric blocks averaging 15 to 25 structural units derived from one or more tetra-alkyl alkylidene bisphenols, the units being joined together through carbonate linkages. These polymeric blocks are, in turn, attached to each other through one or more coupling radicals selected from the class (a), (b), or (c), (d) or (e) set forth above.

The carbonate polymers of the invention are characterized by heat distortion temperatures of at least  $150^\circ\text{C}$ . Generally speaking, the polymeric carbonate of the invention containing homopolymeric blocks averaging 15 to 25 structural units derived from 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-propane linked together through carbonate groups, said blocks being bonded to each other through bisphenol-A carbonate units, are characterized by an intrinsic viscosity measured in *p*-dioxane at  $30.3^\circ\text{C}$ ., of at least 0.40.

The hydrolytic stability of the polycarbonates of the invention is truly remarkable as compared with the polycarbonates of the prior art. For example, a part molded of bisphenol-A polycarbonate loses 30% of its weight after remaining in a 10% aqueous sodium hydroxide solution for five days at reflux conditions. Parts formed of the polycarbonate prepared from 2,2 bis-(3-methyl-4-hydroxyphenyl)-propane were found to lose 2% of their weight after two days under similar conditions. On the other hand, parts molded of the polycarbonates of the invention lost no weight at all after five days at reflux in a 10% aqueous sodium hydroxide solution.

The following examples are given by way of illustration. Viscosities are reported in deciliters per gram measured in *p*-dioxane at  $30.3^\circ\text{C}$ .

## EXAMPLE 1

5 A solution of 21 grams of 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane [hereafter designated as TMBPA] in 350 ml. of methylene chloride and 50 grams of pyridine was phosgenated at the rate of 0.3 gram per minute for 40 minutes. After stirring for 42 minutes, the solution was again phosgenated at a rate of 0.3 gram per minute for 17 minutes, then stirred for 29 minutes and finally phosgenated at a rate of 0.1 gram per minute for 11 minutes, to provide a relatively low molecular weight (intrinsic viscosity 0.28) polycarbonate. The resulting reaction mixture was diluted with sufficient methylene chloride to provide a total volume of 500 ml. which was divided into five 100 ml. aliquot samples. A different difunctional reactant was then added to each of four of these samples, the fifth sample being used as the control. Addition of the difunctional compound was accomplished by first dissolving the compound in 1 ml. of pyridine and 10 ml. of methylene chloride. The resulting solution was then added to the 100 ml. sample containing the low molecular weight polycarbonate. The resulting high molecular weight polymeric carbonate which formed was precipitated and washed with methanol. The control sample was precipitated and the low molecular weight polymer washed in the same manner. The data obtained are set forth in Table I below:

TABLE I

Sample	Coupling Agent	Amount Polymer Used (Grams)	Yield (Grams)	Reduced Viscosity
B	2,2-bis-(3-methyl-4-hydroxyphenyl)-propane	0.64	15.5	0.65
C	2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane	1.36	16.	1.13
D	Hydroquinone	0.28	15.5	0.59
E	Control		9.5	0.28

20 The following examples illustrate the use of 2,2-bis-(4-hydroxyphenyl)-propane as the difunctional reactant in the production of the polymeric carbonates of the invention.

## EXAMPLE 2

25 A solution of 71 g. of TMBPA in 280 ml. of methylene chloride and 50 g. of pyridine was phosgenated at a rate of 0.5 g. per minute for 48 minutes. After a period of 24 minutes, phosgenation at 0.5 g. per minute was resumed for nine minutes. After stirring for 15 minutes, 40 ml. of a solution of 2,2-bis(4-hydroxyphenyl)-propane [hereafter referred to as BPA] in 10 ml. of pyridine and enough methylene chloride to make the solution up to 100 ml. was added dropwise over an 80-minute period. The solution became so viscous that stirring became difficult. A solution of 18 ml. of concentrated hydrochloric acid in 100 ml. of water was added, and the polymer was precipitated, washed with methanol, and dried. A fibrous solid  $\eta_i=1.00$ , 68 g., was obtained.

## EXAMPLE 3

35 A solution of 56.8 g. of TMBPA in 37.6 g. of pyridine and 379 g. of methylene chloride was phosgenated at a rate of 0.5 g. per minute for 40 minutes, stirred for 15 minutes and then phosgenated at a rate of 0.5 g. per minute for an additional 10 minutes. Thereafter, a solution of 11.4 g. of BPA in 9.5 g. of pyridine and 76 g. of methylene chloride was added and the resulting solution was phosgenated at a rate of 0.5 g. per minute for 20 minutes. The resulting polymer was precipitated, washed with methanol and dried. 68.3 g. of the high molecular weight polymeric carbonate in the form of a powder, having an intrinsic viscosity of 0.62, was thus obtained.

## EXAMPLE 4

45 A solution of 42.6 g. of TMBPA in 30 g. of pyridine and 200 ml. of methylene chloride was phosgenated at a rate of 0.5 g. per minute for 25 minutes, stirred for 15 minutes, then phosgenated at 0.5 g. per minute for 5 minutes, stirred again for

15 minutes and re-phosgenated for an additional 10 minutes. A solution of 22.8 g. of BPA in 20 g. of pyridine and 76 g. of methylene chloride was added. The resulting solution was phosgenated at 0.5 g. per minute for 30 minutes. The high molecular weight polymeric carbonate formed was precipitated, washed with methanol and dried. 65 g. of the polymer in powder form having an intrinsic viscosity of 0.88 was thus obtained.

The heat distortion temperatures of the polymers of Examples 5—11 are, respectively, 204, 215, 196, 211, 198, 207 and 190° C.

#### EXAMPLE 5

This example illustrates the use of 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane in the preparation of a polymeric carbonate of the invention.

A solution of 71 g. of TMBPA in 200 ml. of methylene chloride and 50 g. of pyridine was phosgenated intermittently at a rate of 0.5 g. per minute, over 125 minutes, until no temperature rise occurred when phosgene was added. After stirring for 15 minutes, 140 ml. of a solution of 35.2 g. of 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane (TCBPA hereafter) in 20 ml. pyridine and enough methylene chloride to make the solution volume 220 ml. was added dropwise over 210 minutes. A solution of 18 ml. of concentrated hydrochloric acid in 100 ml. of water was added, and the polymer was precipitated, washed with methanol and dried. The high molecular weight polymeric carbonate thus obtained had a reduced viscosity of 1.23 in dioxane at 30° and 0.4 g/dl. concentration.

#### EXAMPLE 6

This example demonstrates the use of a dihydroxyaryl sulfone in the production of a polymeric carbonate of the invention.

A solution of 71 g. TMBPA in 200 ml. of methylene chloride and 50 g. of pyridine was phosgenated intermittently at a rate of 0.5 g. per minute, over 125 minutes, until no temperature rise occurred when phosgene was added. After stirring for 60 minutes, a solution of 14.7 g. of 3,3', 5,5'-tetramethyl-4,4'-dihydroxydiphenyl-sulfone [hereafter referred to as DXS] in 100 ml. of pyridine was added dropwise over 120 minutes. It was necessary to add 200 ml. of methylene chloride during the addition of the DXS so stirring could be continued. A solution of 18 ml. of concentrated hydrochloric acid in 100 ml. of water was added, and the polymer was precipitated, washed with methanol, and dried. The resulting high molecular weight polymeric carbonate had a reduced viscosity of 1.16 in dioxane at 30° and 0.4 g/dl. concentration.

#### EXAMPLE 7

This example illustrates the use of 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane in the practice of the invention.

A solution of 71 g. TMBPA in 200 ml. of methylene chloride and 50 g. of pyridine was phosgenated intermittently at a rate of 0.5 g. per minute, over 190 minutes, until no temperature rise occurred when phosgene was added. After stirring for 15 minutes, 125 ml. of a solution of 24.6 g. 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane [hereafter referred to as BPC] in 20 ml. of pyridine and enough methylene chloride to make the solution volume 200 ml. was added dropwise over 154 minutes. It was necessary to add 200 ml. of methylene chloride during the addition of the BPC solution to aid stirring. A solution of 18 ml. of concentrated hydrochloric acid in 100 ml. of water was added, and the polymer was precipitated, washed with methanol, and dried. The polymer thus obtained had a reduced viscosity of 0.54 in dioxane at 30° and 0.4 g/dl. concentration.

#### EXAMPLE 8

This example demonstrates the use of 3,3-bis-(4-hydroxyphenyl)-pentane in the practice of the invention.

A solution of 71 g. TMBPA in 200 ml. of methylene chloride and 50 g. of pyridine was phosgenated intermittently at a rate of 0.5 g. per minute, over 70 minutes, until no temperature rise occurred when phosgene was added. After stirring 45 minutes, a solution of 24.6 g. 3,3-bis-(4-hydroxyphenyl)-pentane (BPP hereafter) in 20 ml. pyridine and sufficient methylene chloride to make the solution volume 200 ml. was added dropwise over 218 minutes. Methylene chloride, 100 ml. had to be added during BPP addition to aid stirring. A solution of 18 ml. of concentrated hydrochloric acid in 100 ml. of water was added, and the polymer was precipitated,

washed with methanol, and dried. The high molecular weight polymeric carbonate thus obtained had a reduced viscosity of 0.67 in dioxane at 30° and 0.4 g/dl. concentration.

#### EXAMPLE 9

This Example illustrates the use of a dihydroxydiphenyl in the practice of the invention.

A solution of 63.9 g. TMBPA in 42.6 g. pyridine and 426 g. methylene chloride was phosgenated at 0.5 g. per minute for 40 minutes, stirred for 15 minutes and then phosgenated at 0.5 g. per minute for 10 minutes. A solution of 9.4 g. p,p'-dihydroxydiphenyl in 9.6 g. pyridine and 48 g. methylene chloride was added dropwise until a temperature drop occurred. The solution was phosgenated at 0.25 g. per minute until the temperature dropped. Addition of the dihydroxydiphenyl solution was continued but was interrupted by two more periods of phosgene addition. A solution of 10 ml. of concentrated hydrochloric acid in 100 ml. of water was added, and the polymer was precipitated, washed with methanol, and dried. The high molecular weight polymeric carbonate thus obtained (67.4 g.) had an intrinsic viscosity of 1.04.

#### EXAMPLE 10

This example demonstrates the use of a dihydroxy-diphenyl ether in the production of the hydrolytically stable polymeric carbonate of the invention.

A solution of 63.9 g. TMBPA in 42.6 g. pyridine and 426 g. methylene chloride was phosgenated at a rate of 0.5 g. per minute for 45 minutes, stirred for 15 minutes and then phosgenated at 0.5 g. per minute for 10 minutes. Subsequently a solution of 10.2 g. 4,4'-dihydroxydiphenyl ether in 9.6 g. pyridine and 48 g. methylene chloride was added dropwise. After 40% had been added, the solution was phosgenated at 0.25 g. per minute until the temperature dropped. Addition of the solution was continued until 75% had been added. After a final phosgenation at 0.25 g. per minute until the temperature dropped, a solution of 10 ml. of concentrated hydrochloric acid in 100 ml. of water was added. The polymer was precipitated, washed with methanol, and dried. The high molecular weight polymeric carbonate thus obtained (68.5 g.) had an intrinsic viscosity of 0.79.

The following two examples demonstrate the use of tetra-alkyl alkylidene bisphenols other than TMBPA in the production of the polymeric carbonates of the invention:

#### EXAMPLE 11

A solution of 25 g. 2,2-bis-(3,5-diisopropyl-4-hydroxyphenyl)-propane in 11 g. pyridine and 70 ml. methylene chloride was phosgenated intermittently at a rate of 0.2 g. per minute, over 113 minutes, until no temperature rise occurred when phosgene was added. A solution of 2.5 g. BPA in 3 ml. pyridine and 30 ml. methylene chloride was added dropwise. The solution was then phosgenated at 0.2 g. per minute for 16 minutes. A solution of 1.5 g. BPA in 2 ml. pyridine and 10 ml. methylene chloride was added dropwise. Another solution of 5 g. BPA in 5 ml. of pyridine and enough methylene chloride to make the volume 30 ml. was added in 3—5 ml. portions. After each addition, the solution was phosgenated at 0.1 g. per minute until the temperature dropped. After 14 ml. of the last solution had been added, 10 ml. of concentrated hydrochloric acid in 20 ml. water was added. The polymer was precipitated, washed with methanol, and dried. The high molecular weight polymeric carbonate thus obtained (30 g.) had an intrinsic viscosity of 0.41.

#### EXAMPLE 12

A solution of 39 g. 3,3-bis-(3,5-dimethyl-4-hydroxyphenyl)-pentane in 25 g. pyridine and 125 ml. methylene chloride was phosgenated intermittently at a rate of 0.5 g. per minute, over 52 minutes, until no temperature rise occurred when phosgene was added. After stirring 5 minutes, 35 ml. of a solution of 5 g. of BPA in 5 ml. pyridine and enough methylene chloride to make the solution volume 50 ml. was added. A solution of 20 ml. of concentrated hydrochloric acid in 100 ml. of water was added, and the polymer was precipitated, washed with methanol, and dried. The high molecular weight polymeric carbonate thus obtained (42 g.) had an intrinsic viscosity of 0.51.

The hydrolytic stability of the polymeric carbonates of the invention was measured by placing two compression molded chips of a sample of the various polymers of the foregoing examples in a pint screw cap jar containing 100 ml. of a 10% sodium hydroxide solution in water. The temperature of the sodium hydroxide solution was maintained at 90° C. throughout the test period. The chips were weighed

before being placed in the solution and were periodically withdrawn, washed and weighed. The results obtained are set forth in Table II below.

TABLE II

Polymer Used	Per Cent Weight Lost After 20 Days
Bisphenol-A polycarbonate (control)	Totally degraded
Bisphenol-C polycarbonate (control)	25
Polymer from Example 2	0
" " " 3	0
" " " 4	0.1

5 The tensile heat distortion temperatures, measured under a 50 psi load, of various polymers of the foregoing examples were measured and compared with the heat distortion temperatures of bisphenol-A polycarbonate and bisphenol-C polycarbonate. The data obtained are set forth in Table III below.

TABLE III

Polymer Tested	Tensile Heat Distortion (°C.)
Bisphenol-A polycarbonate	149
Bisphenol-C polycarbonate	110
Polycarbonate from Example 1 (Sample B)	196
" " " 1 (Sample C)	207
" " " 1 (Sample D)	189
" " " 2	212
" " " 3	193
" " " 4	194

10 The tensile properties of various polymeric carbonates of the invention were measured. The results obtained are set forth in Table IV below.

TABLE IV

Polymer Tested	Modulus (psi)	Yield Strength (psi)	Ultimate Tensile Strength (psi)	Elong- ation %
Polymer from Example 2	$1.99 \times 10^5$	$11.0 \times 10^3$	$9.9 \times 10^3$	15
" " " 3	$2.36 \times 10^5$	$12.8 \times 10^3$	$9.8 \times 10^3$	46
" " " 4	$2.47 \times 10^5$	$13.6 \times 10^3$	—	9

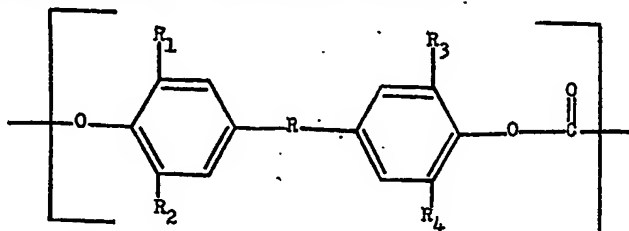
The present invention thus provides a new class of polymeric aromatic carbonates

having a high degree of hydrolytic stability and a high heat distortion temperature. Such polymeric carbonates may be used in molding compound formulations alone or in combination with fillers such as, for example, wood flour, diatomaceous earth, silica, carbon black, glass fibers, and with pigments to make molded parts of various shapes. They are useful in preparing injection molded or extruded parts, including gaskets, tubing, pipe and other materials which have an improved hydrolytic stability and high heat distortion temperature. Films of the polymeric carbonate of the invention are useful as wrapping or packaging materials, as metal liners, electrical capacitor dielectrics, sound recording tapes and pipe coverings.

Film and fibers of the polymeric carbonates of the invention may be beneficially oriented or drawn at elevated temperatures. Fibers of such polymeric carbonate materials may be used for yarn, thread, bristles and rope and are readily dyed. The polymeric carbonates of the invention may also be admixed with other resin materials.

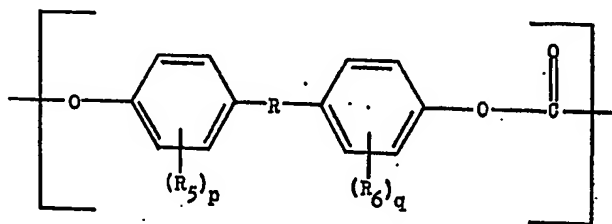
**WHAT WE CLAIM IS:—**

1. A high molecular weight, hydrolytically stable, polymeric aromatic carbonate having a heat distortion temperature of at least 150° C. and containing in its linear chain a major proportion of structural units of the formula

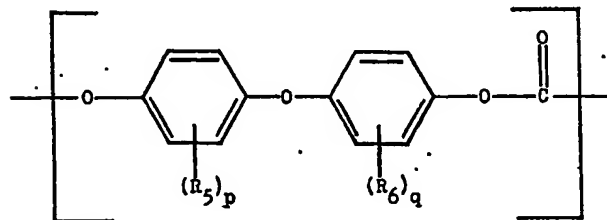


and a minor proportion of structural units of the formula

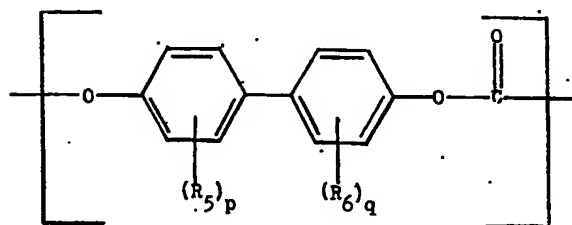
(a)



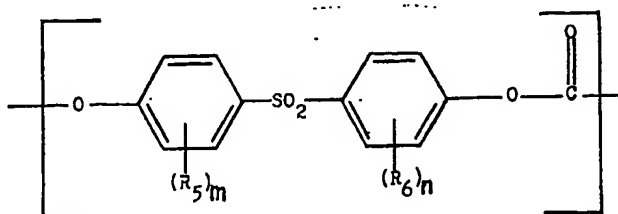
(b)



(c)

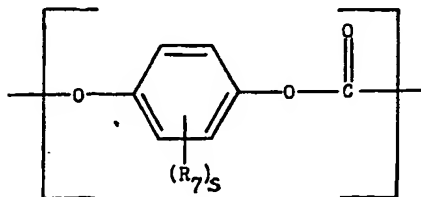


(d)



or

(e)



where

R is an alkylidene radical containing from 1 to 10 carbon atoms or a cyclo-alkylidene radical containing from 5 to 8 carbon atoms in the cyclic ring;

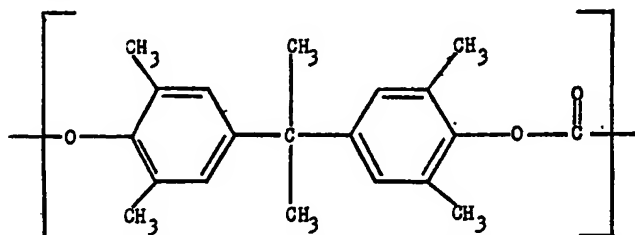
R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> may be the same or different and each is an alkyl radical containing from 1 to 3 carbon atoms;

R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> may be the same or different and each is halogen or an alkyl radical containing from 1 to 3 carbon atoms;

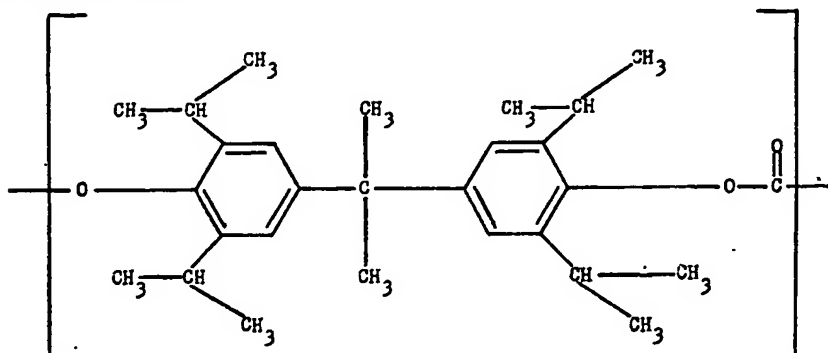
each of p and q is 0, 1 or 2 except that where R<sub>5</sub> and R<sub>6</sub> are both alkyl, each of p and q is 0 or 1; and

each of m, n and s is 0, 1 or 2.

2. A polymer according to Claim 1, wherein the major proportion of the structural units has the formula

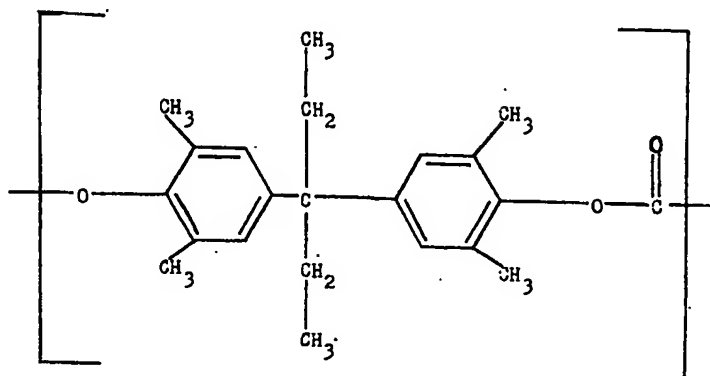


3. A polymer according to Claim 1, wherein the major proportion of the structural units has the formula

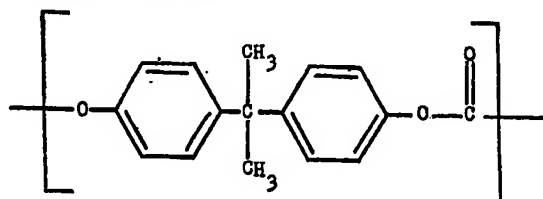


4. A polymer according to Claim 1, wherein the major proportion of the structural units has the formula





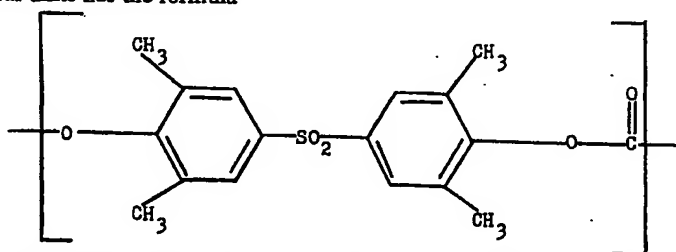
5. A polymer according to any one of Claims 1—4, wherein the minor proportion of the structural units has the formula



5

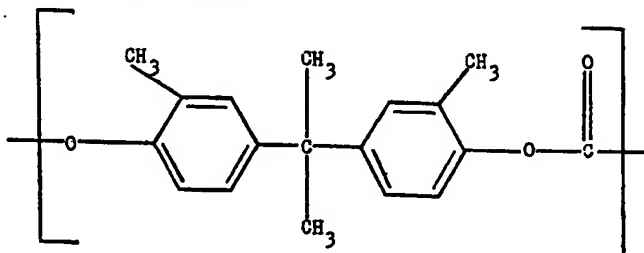
6. A polymer according to Claim 1, 2 or 3, wherein the minor proportion of the structural units has the formula

5



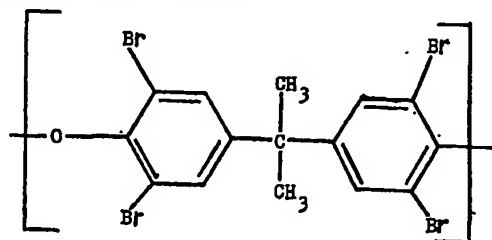
7. A polymer according to any one of Claims 1—4, wherein the minor proportion of the structural units has the formula

10

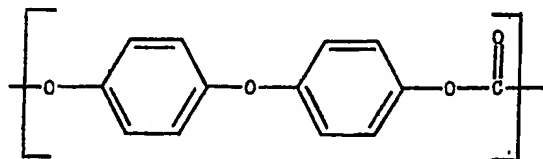


10

8. A polymer according to any one of Claims 1—4, wherein the minor proportion of the structural units has the formula

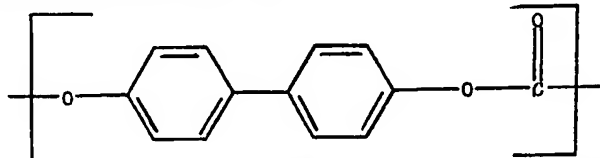


9. A polymer according to any one of Claims 1—4, wherein the minor proportion of the structural units has the formula



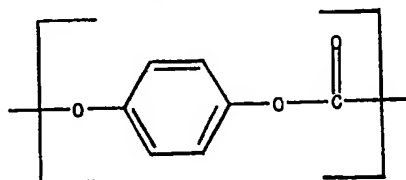
5

10. A polymer according to any one of Claims 1—4, wherein the minor proportion of the structural units has the formula



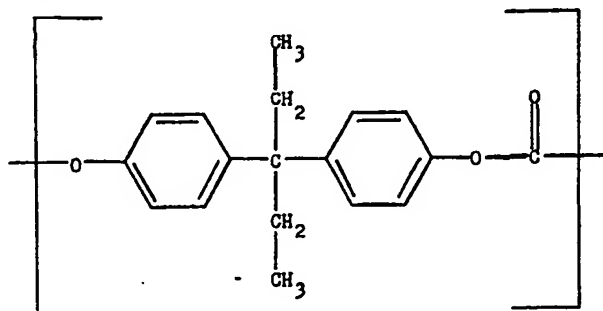
5

11. A polymer according to any one of Claims 1—4, wherein the minor proportion of the structural units has the formula



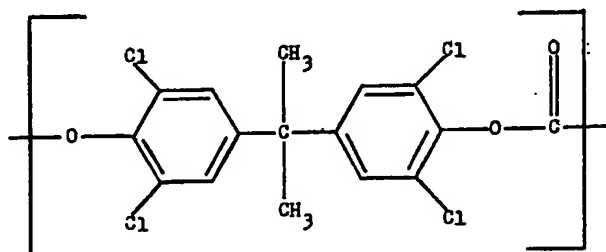
10

12. A polymer according to any one of Claims 1—4, wherein the minor proportion of the structural units has the formula



10

13. A polymer according to any one of Claims 1—4, wherein the minor proportion of the structural units has the formula

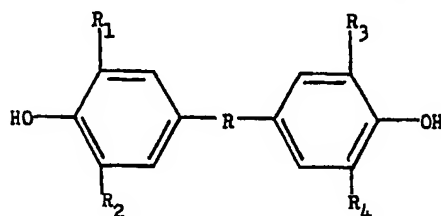


15

15

14. A process for the production of a polymer as claimed in Claim 1, which comprises reacting, in an inert organic solvent containing an acid acceptor, a molar

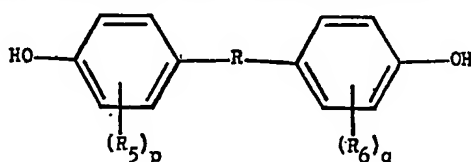
excess of a carbonyl halide with a tetra-alkyl alkylidene bisphenol of the formula



where

R is an alkylidene radical containing from 1 to 10 carbon atoms, or a cyclo-alkylidene radical containing from 5 to 8 carbon atoms in the cyclic ring, and

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are as defined in Claim 1, to provide a low molecular weight carbonate polymer of said tetra-alkyl alkylidene bisphenol, and subsequently reacting said low molecular weight carbonate polymer with a dihydric phenol capable of reacting therewith in the presence of sufficient carbonyl halide necessary to complete the reaction to the desired extent, said phenol having the formula

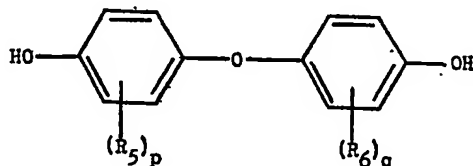


where

R has the meaning given in Claim 1, each of

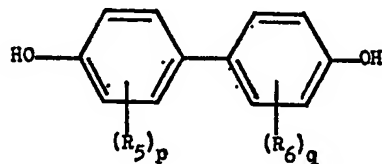
R<sub>5</sub> and R<sub>6</sub> is selected from halogen and alkyl radicals containing up to three carbon atoms, each of

p and q is 0, 1 or 2, except that when R<sub>5</sub> and R<sub>6</sub> are both alkyl, p and q are no greater than 1,



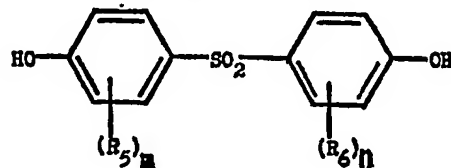
where

R<sub>5</sub>, R<sub>6</sub>, p and q all have the meanings given above,



where

R<sub>5</sub>, R<sub>6</sub>, p and q all have the meanings given above,

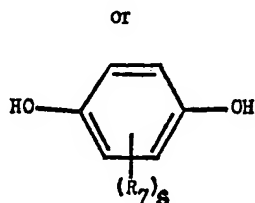


25

where

R<sub>5</sub> and R<sub>6</sub> have the meanings given above and each of m and n is 0, 1 or 2,

25



where

$\text{R}_7$  is selected from halogen and alkyl radicals containing from 1 to 3 carbon atoms, and

$s$  is 0, 1 or 2.

15. A process according to Claim 14, substantially as herein described with reference to any one of the Examples.

16. A high molecular weight, hydrolytically stable, polymeric aromatic carbonate whenever produced by the process claimed in Claim 14 or 15.

17. The specific polymeric aromatic carbonates according to Claim 1 produced in any one of the foregoing Examples.

18. Moulding compound formulations consisting of the polymeric aromatic carbonates claimed in any one of Claims 1 to 13, 16 and 17.

19. Moulding compound formulations comprising polymeric aromatic compounds according to Claim 18 together with wood flour, diatomaceous earth, silica, carbon black, glass fibers, pigments or other fillers.

20. Gaskets, tubing, pipes or other extruded parts made of the molding compounds claimed in either one of Claims 18 or 19.

21. Wrapping or packaging films, metal liners, electrical capacitor dielectrics, sound recording tapes and pipe coverings made of the polycarbonates claimed in any one of Claims 1 to 13, 16 and 17.

22. Oriented or drawn films and fibers made from the polymeric carbonates claimed in any one of Claims 1 to 13, 16 and 17.

23. Yarn, thread, bristles and rope made of the fibers claimed in Claim 22.

For the Applicants:—

G. H. MUNSTER & CO.,

Chartered Patent Agents,

Imperial Buildings, 56 Kingsway, London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.  
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

**POOR QUALITY**

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ ~~FADED TEXT OR DRAWING~~
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ ~~LINES OR MARKS ON ORIGINAL DOCUMENT~~
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**